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* * * * * * * * * * Welcome to STN International * * * * * * * * * *

NEWS 1		Web Page URLs for STN Seminar Schedule - N. America
NEWS 2		"Ask CAS" for self-help around the clock
NEWS 3	AUG 09	INSPEC enhanced with 1898-1968 archive
NEWS 4	AUG 28	ADISCTI Reloaded and Enhanced
NEWS 5	AUG 30	CA(SM)/CAplus(SM) Austrian patent law changes
NEWS 6	SEP 11	CA/CAplus enhanced with more pre-1907 records
NEWS 7	SEP 21	CA/CAplus fields enhanced with simultaneous left and right truncation
NEWS 8	SEP 25	CA(SM)/CAplus(SM) display of CA Lexicon enhanced
NEWS 9	SEP 25	CAS REGISTRY(SM) no longer includes Concord 3D coordinates
NEWS 10	SEP 25	CAS REGISTRY(SM) updated with amino acid codes for pyrrolysine
NEWS 11	SEP 28	CEABA-VTB classification code fields reloaded with new classification scheme
NEWS 12	OCT 19	LOGOFF HOLD duration extended to 120 minutes
NEWS 13	OCT 19	E-mail format enhanced
NEWS 14	OCT 23	Option to turn off MARPAT highlighting enhancements available
NEWS 15	OCT 23	CAS Registry Number crossover limit increased to 300,000 in multiple databases
NEWS 16	OCT 23	The Derwent World Patents Index suite of databases on STN has been enhanced and reloaded
NEWS 17	OCT 30	CHEMLIST enhanced with new search and display field
NEWS 18	NOV 03	JAPIO enhanced with IPC 8 features and functionality
NEWS 19	NOV 10	CA/CAplus F-Term thesaurus enhanced
NEWS 20	NOV 10	STN Express with Discover! free maintenance release Version 8.01c now available
NEWS 21	NOV 13	CA/CAplus pre-1967 chemical substance index entries enhanced with preparation role
NEWS 22	NOV 20	CAS Registry Number crossover limit increased to 300,000 in additional databases
NEWS 23	NOV 20	CA/CAplus to MARPAT accession number crossover limit increased to 50,000
NEWS 24	NOV 20	CA/CAplus patent kind codes will be updated

NEWS EXPRESS	NOVEMBER 10 CURRENT WINDOWS VERSION IS V8.01c, CURRENT MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP), AND CURRENT DISCOVER FILE IS DATED 25 SEPTEMBER 2006.
NEWS HOURS	STN Operating Hours Plus Help Desk Availability
NEWS LOGIN	Welcome Banner and News Items
NEWS IPC8	For general information regarding STN implementation of IPC 8
NEWS X25	X.25 communication option no longer available

Enter NEWS followed by the item number or name to see news on that specific topic.

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* * * * * * * * * * * * * * * * STN  Columbus  * * * * * * * * * * * * * * * * *

FILE 'HOME' ENTERED AT 10:45:43 ON 01 DEC 2006

=> file casreact
COST IN U.S. DOLLARS                                    SINCE FILE      TOTAL
                                                           ENTRY     SESSION
FULL ESTIMATED COST                                         0.21        0.21

FILE 'CASREACT' ENTERED AT 10:46:04 ON 01 DEC 2006
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FILE CONTENT:1840 - 27 Nov 2006 VOL 145 ISS 22

New CAS Information Use Policies, enter HELP USAGETERMS for details.

************************************************************
*                                                          *
*     CASREACT now has more than 10 million reactions      *
*                                                          *
************************************************************

Some CASREACT records are derived from the ZIC/VINITI database (1974-1991)
provided by InfoChem, INPI data prior to 1986, and Biotransformations
database compiled under the direction of Professor Dr. Klaus Kieslich.

This file contains CAS Registry Numbers for easy and accurate substance
identification.

=>
Uploading C:\Program Files\Stnexp\Queries\10735408.str

L1      STRUCTURE UPLOADED

=> d l1
L1 HAS NO ANSWERS
L1              STR
*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

Structure attributes must be viewed using STN Express query preparation.


=> s l1 sss sam
SAMPLE SEARCH INITIATED 10:46:55 FILE 'CASREACT'
SCREENING COMPLETE -     1601 REACTIONS TO VERIFY FROM      114 DOCUMENTS

100.0% DONE    1601 VERIFIED       7 HIT RXNS                      4 DOCS
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS:  ONLINE  **COMPLETE**
                        BATCH   **COMPLETE**
PROJECTED VERIFICATIONS:     29623 TO    34417
PROJECTED ANSWERS:               4 TO      199

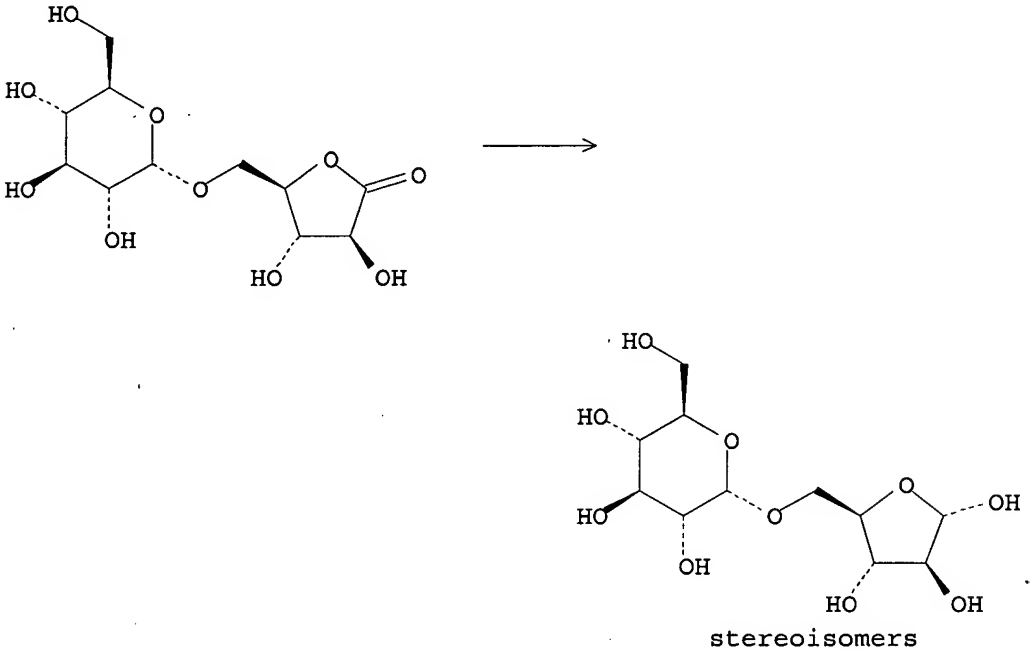
L2            4 SEA SSS SAM L1 (     7 REACTIONS)
```

=> d scan

L2 4 ANSWERS CASREACT COPYRIGHT 2006 ACS on STN

TI Disaccharide building blocks from isomaltulose: glucosyl-α(1→5)-D-arabinonic acid and ensuing products

RX(3) OF 6



stereoisomers

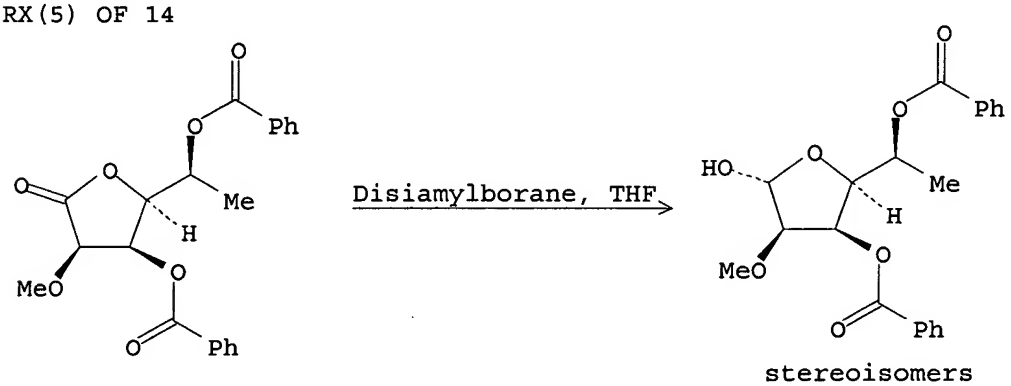
NOTE: 2 steps

HOW MANY MORE ANSWERS DO YOU WISH TO SCAN? (1):1

L2 4 ANSWERS CASREACT COPYRIGHT 2006 ACS on STN

TI The use of aldonolactones for the synthesis of 2-O-methyl-L-rhamnose and 2-O-methyl-D-mannose

RX(5) OF 14



stereoisomers

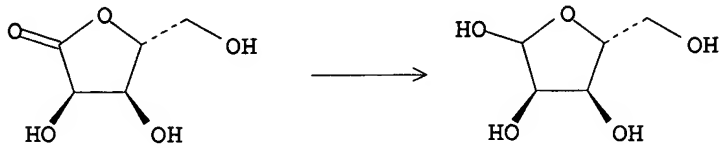
97%

HOW MANY MORE ANSWERS DO YOU WISH TO SCAN? (1):1

L2 4 ANSWERS CASREACT COPYRIGHT 2006 ACS on STN

TI Preparation of D-ribose from D-ribono-γ-lactone

RX(1) OF 1



HOW MANY MORE ANSWERS DO YOU WISH TO SCAN? (1):end

```
=> s l1 sss full
FULL SEARCH INITIATED 10:50:58 FILE 'CASREACT'
SCREENING COMPLETE -    28991 REACTIONS TO VERIFY FROM     2093 DOCUMENTS

100.0% DONE   28991 VERIFIED      70 HIT RXNS                      26 DOCS
SEARCH TIME: 00.00.03

L3           26 SEA SSS FUL L1 (    70 REACTIONS)

=> s l3 and (NaHTe or SmI2)
            32 NAHTE
           924 SMI2
L4           0 L3 AND (NAHTE OR SMI2)

=> s l3 and tellurohydride
             0 TELLUROHYDRIDE
L5           0 L3 AND TELLUROHYDRIDE

=> s l3 and (samarium(a)iodide)
          2406 SAMARIUM
             3 SAMARIUMS
          2406 SAMARIUM
                 (SAMARIUM OR SAMARIUMS)
         24362 IODIDE
          4436 IODIDES
         25885 IODIDE
                 (IODIDE OR IODIDES)
           598 SAMARIUM(A)IODIDE
L6           0 L3 AND (SAMARIUM(A)IODIDE)

=> s l3 and (hydrogen(a)palladium(a)phosphine)
         34904 HYDROGEN
           651 HYDROGENS
         35338 HYDROGEN
                 (HYDROGEN OR HYDROGENS)
         23706 PALLADIUM
             6 PALLADIUMS
         23706 PALLADIUM
                 (PALLADIUM OR PALLADIUMS)
         15380 PHOSPHINE
          4762 PHOSPHINES
         16636 PHOSPHINE
                 (PHOSPHINE OR PHOSPHINES)
             0 HYDROGEN(A)PALLADIUM(A)PHOSPHINE
L7           0 L3 AND (HYDROGEN(A)PALLADIUM(A)PHOSPHINE)

=> s l3 and (hydrogen(a)catalyst)
```

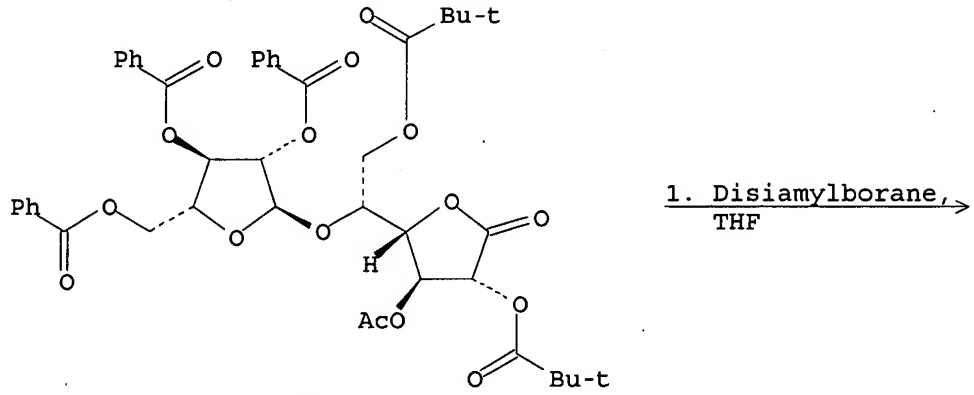
```
          34904 HYDROGEN
            651 HYDROGENS
          35338 HYDROGEN
                  (HYDROGEN OR HYDROGENS)
          84032 CATALYST
          78456 CATALYSTS
         100975 CATALYST
                  (CATALYST OR CATALYSTS)
            208 HYDROGEN(A)CATALYST
L8            0 L3 AND (HYDROGEN(A)CATALYST)

=> s l3 and (aluminum(w)t-butoxy(w)hydride)
          12332 ALUMINUM
             14 ALUMINUMS
          12335 ALUMINUM
                  (ALUMINUM OR ALUMINUMS)
          11297 T
           1566 BUTOXY
             20 T-BUTOXY
                  (T(W)BUTOXY)
          17641 HYDRIDE
           1702 HYDRIDES
          18107 HYDRIDE
                  (HYDRIDE OR HYDRIDES)
              0 ALUMINUM(W)T-BUTOXY(W)HYDRIDE
L9            0 L3 AND (ALUMINUM(W)T-BUTOXY(W)HYDRIDE)

=> d l3 FCRDREF

L3   ANSWER 1 OF 26  CASREACT  COPYRIGHT 2006 ACS on STN

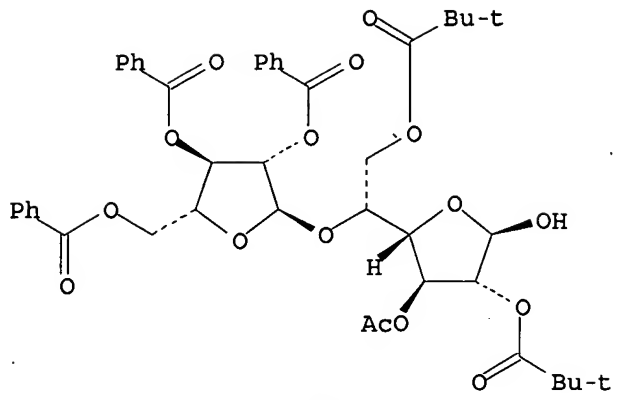
RX(4) OF 28
```



1. Disiamylborane, THF

(step 2)

RX(4) OF 28



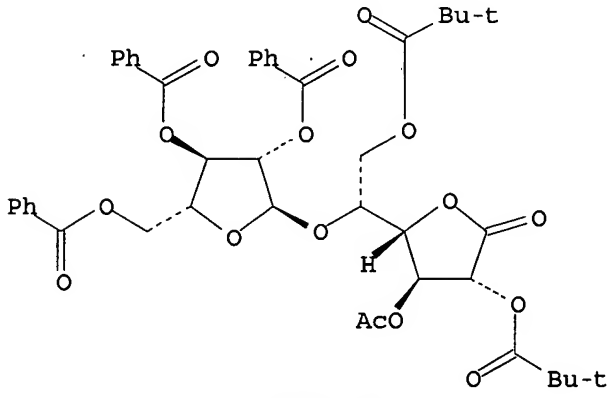
86%

REF: Canadian Journal of Chemistry, 84(4), 486-491; 2006
NOTE: stereoselective
CON: STAGE(1) room temperature -> 0 deg C
STAGE(2) 0 deg C; 22 hours, room temperature

=> d l3 1-26 FCRDREF

L3 ANSWER 1 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

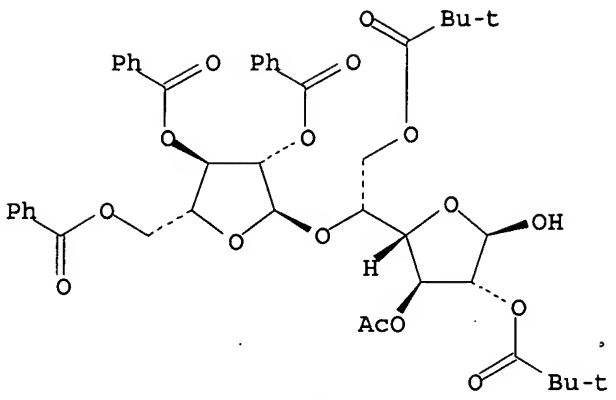
RX(4) OF 28



1. Disiamylborane,
THF

(step 2)

RX(4) OF 28

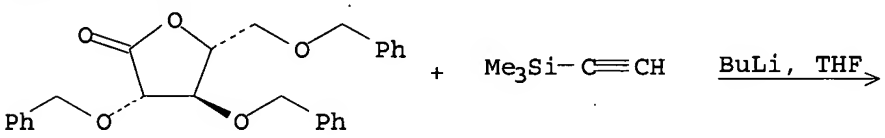


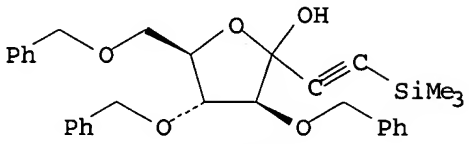
86%

REF: Canadian Journal of Chemistry, 84(4), 486-491; 2006
NOTE: stereoselective
CON: STAGE(1) room temperature -> 0 deg C
STAGE(2) 0 deg C; 22 hours, room temperature

L3 ANSWER 2 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(11) OF 41



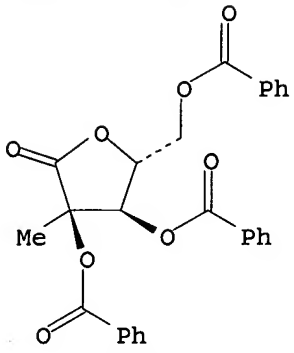


66%

REF: Tetrahedron Letters, 46(18), 3249-3252; 2005
NOTE: stereoselective
CON: -78 deg C

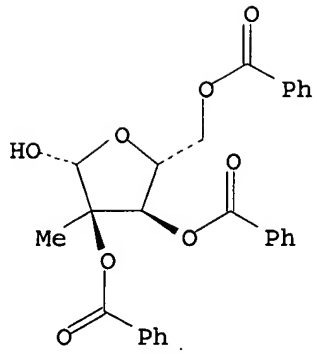
L3 ANSWER 3 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(3) OF 115



(step 2)

1. Red-Al, EtOH, PhMe
3. HCl, Water, Me2CO



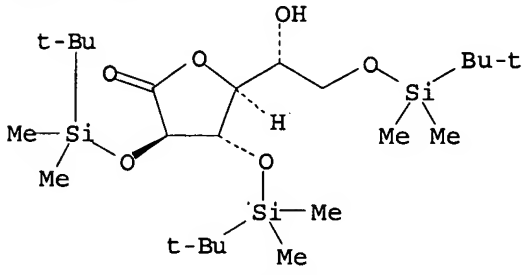
100%

REF: PCT Int. Appl., 2004052899, 24 Jun 2004

CON: STAGE(1) 5 minutes, 0 deg C; 15 minutes, 0 deg C
STAGE(2) 10 minutes; 40 minutes, -5 deg C
STAGE(3) 0 deg C

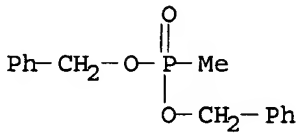
L3 ANSWER 4 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(3) OF 71



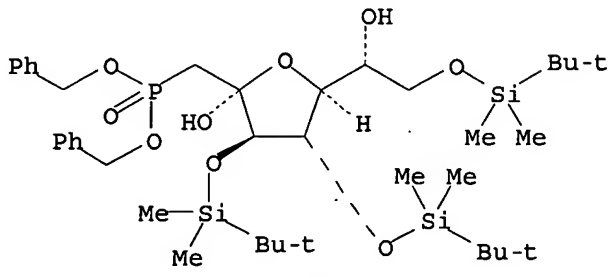
(step 2)

+



(step 1)

1. BuLi, THF, Hexane
2. THF



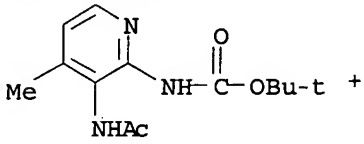
81%

REF: Chemistry--A European Journal, 9(23), 5888-5898; 2003

NOTE: stereoselective, 20:80 alpha:beta
CON: STAGE(1) 20 minutes, -70 deg C
STAGE(2) 10 minutes, -70 deg C; 1 hour, -70 deg C -> -40 deg C

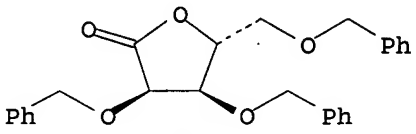
L3 ANSWER 5 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(1) OF 23

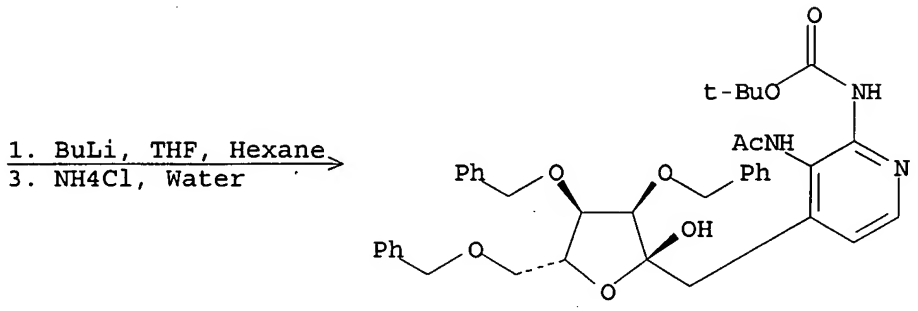


(step 1)

+



(step 2)



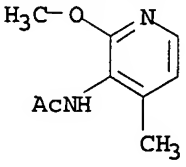
27%

REF: Journal of Organic Chemistry, 68(16), 6466-6469; 2003

NOTE: stereoselective, other product also detected
CON: STAGE(1) 15 minutes, -78 deg C; 20 minutes, -78 deg C -> 5 deg C;
5 deg C -> -78 deg C
STAGE(2) 15 minutes, -78 deg C; 5 hours, room temperature

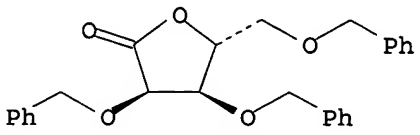
L3 ANSWER 6 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(1) OF 21



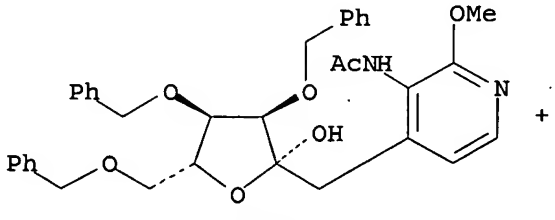
(step 1)

+



(step 2)

1. BuLi, THF
2. THF
3. NH4Cl, Water
4. Water
5. CH2Cl2



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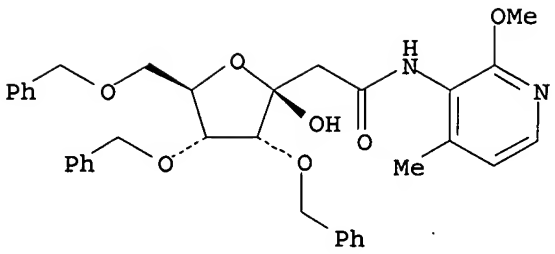
63%

RX(1) OF 21

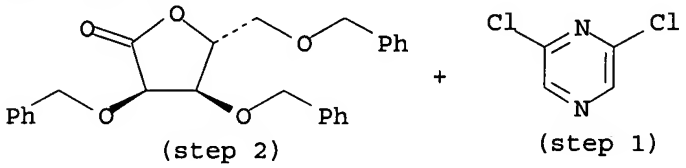


6%

REF: Synlett, (9), 1479-1482; 2002
NOTE: stereoselective
CON: STAGE(1) 15 minutes, -78 deg C; 1 hour, -40 deg C
STAGE(2) 1 hour, -78 deg C

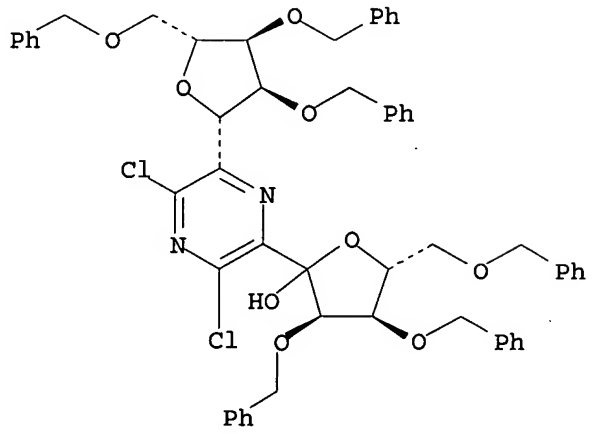
L3 ANSWER 7 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(1) OF 24



(step 2) (step 1)

1. Me4-piperidine, BuLi, THF, Hexane
2. THF
3. NH4Cl, Water



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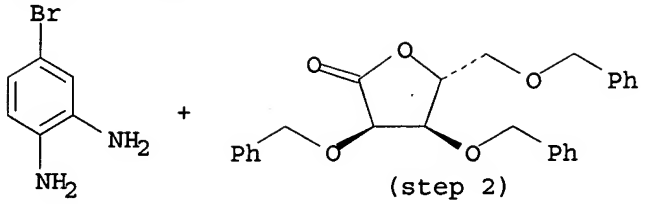
REF: Journal of Organic Chemistry, 66(14), 4783-4786; 2001

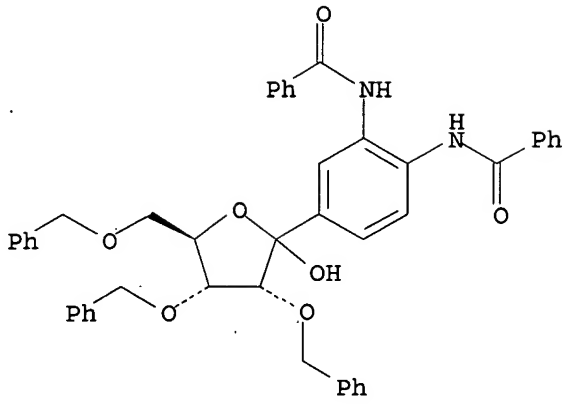
L3 ANSWER 8 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(11) OF 87



(step 1) (step 2)

1. R:13528-93-3, DBU, DMF
2. BuLi, THF
3. PhCOCl, Et3N, CH2Cl2

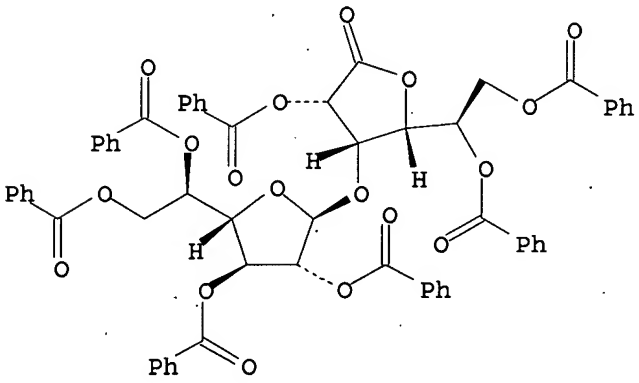


30%

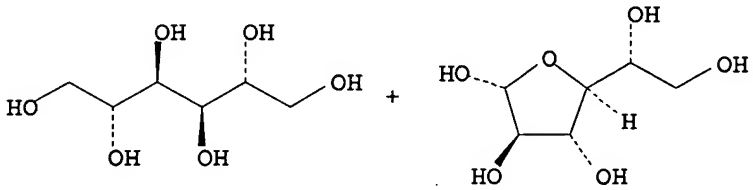
REF: Bulletin of the Chemical Society of Japan, 73(9), 1945-1954; 2000

L3 ANSWER 9 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(15) OF 39 - 2 STEPS



1.1. NaBH4, MeOH
1.2. NaOMe, MeOH
2. C:52357-57-0, Water

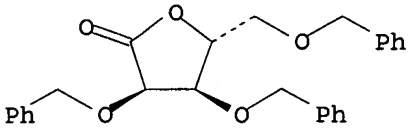


REF: Carbohydrate Research, 311(4), 183-189; 1998

NOTE: 2) stereoselective, enzymic, biotransformation, sodium acetate buffered solution used, beta -D-furanosidase from Penicillium fellutanum used
CON: STEP(1.1) overnight, room temperature
STEP(1.2) 3 hours, room temperature
STEP(2.1) 1.5 hours, 37 deg C, pH 4; 2 minutes, 80 deg C

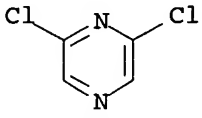
L3 ANSWER 10 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(2) OF 3



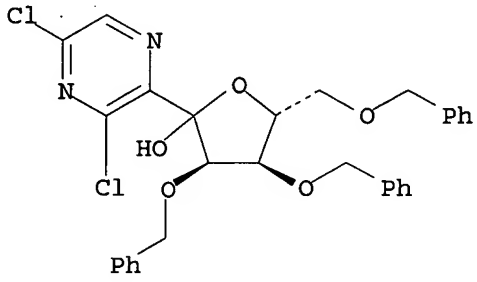
(step 2)

+



(step 1)

1. LiN(Pr-i)2, THF
2. THF
3. BF3-Et2O, Et3SiH, CH2Cl2

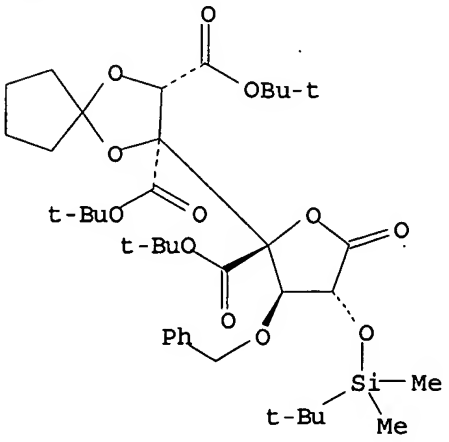


77%

REF: Tetrahedron Letters, 37(30), 5324-5328; 1996
NOTE: key step

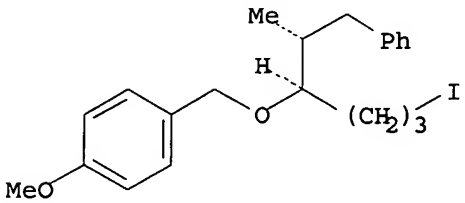
L3 ANSWER 11 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(11) OF 180



(step 2)

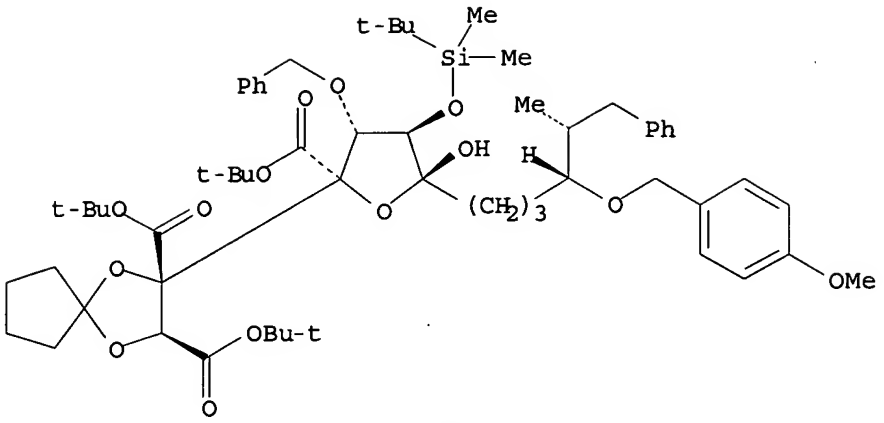
+



(step 1)

1. t-BuLi, Hexane,
Et2O

RX(11) OF 180

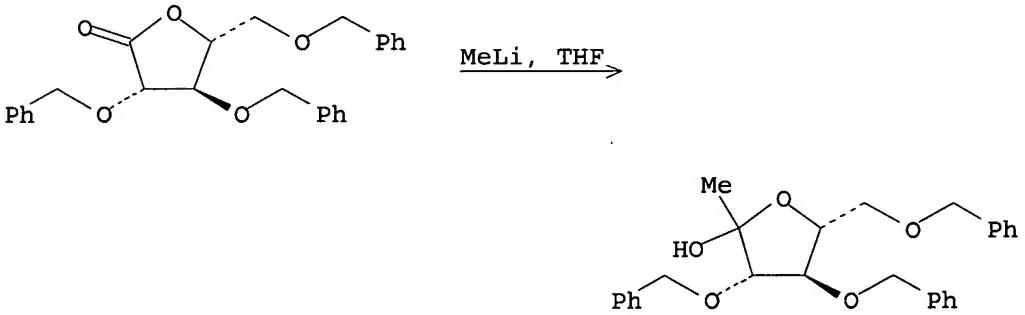


73%

REF: Journal of the American Chemical Society, 116(26), 12111-12; 1994
NOTE: stereoselective

L3 ANSWER 12 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

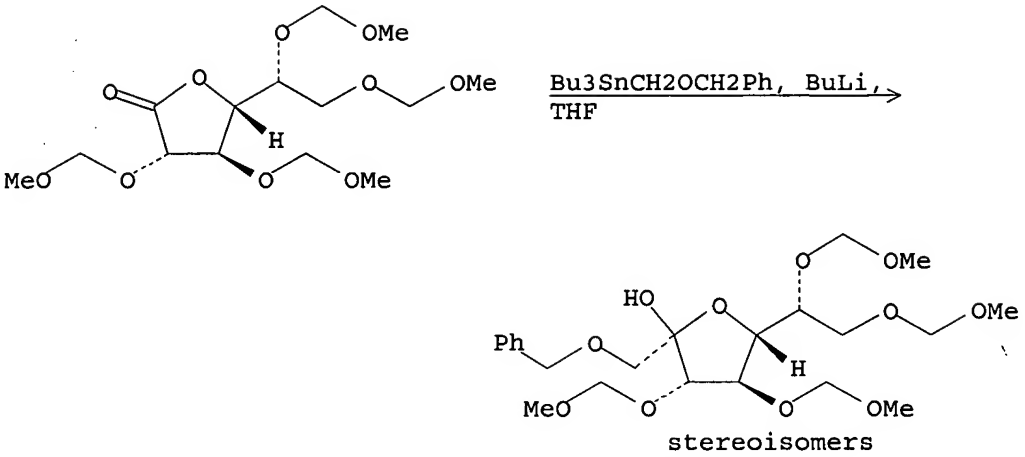
RX(2) OF 33



REF: Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry, (5), 517-18; 1995

L3 ANSWER 13 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

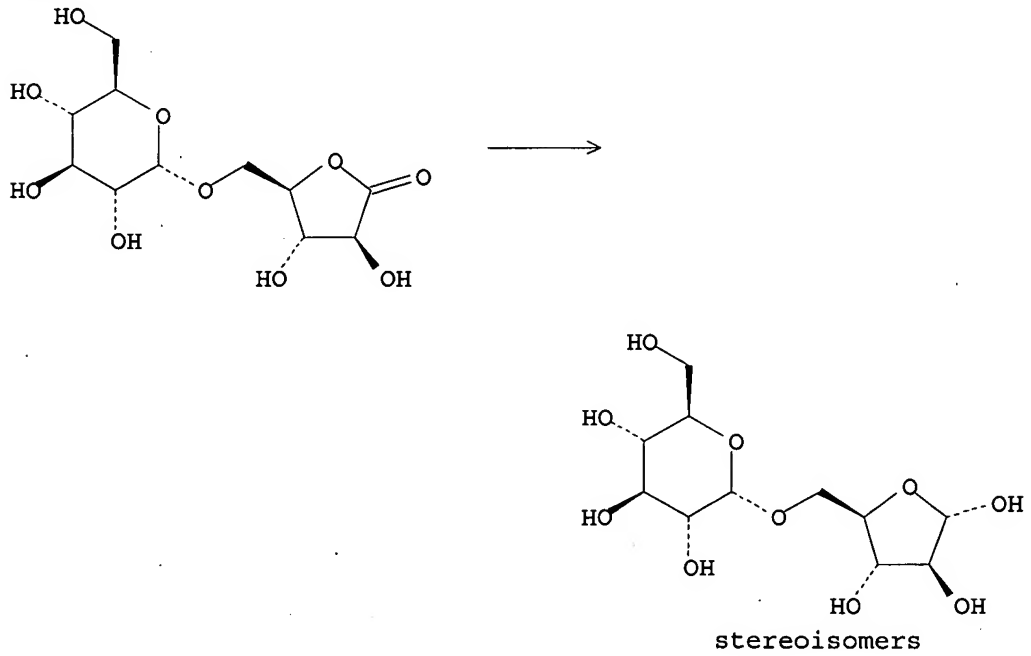
RX(4) OF 22



REF: Carbohydrate Research, 253,, 195-206; 1994
NOTE: KEY STEP; 81% OVERALL

L3 ANSWER 14 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

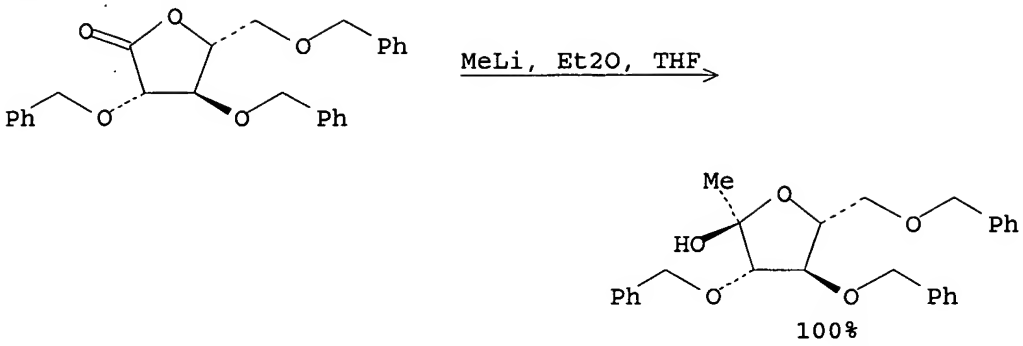
RX(3) OF 6



REF: Liebigs Annalen der Chemie, (9), 975-80; 1993
NOTE: 2 steps

L3 ANSWER 15 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

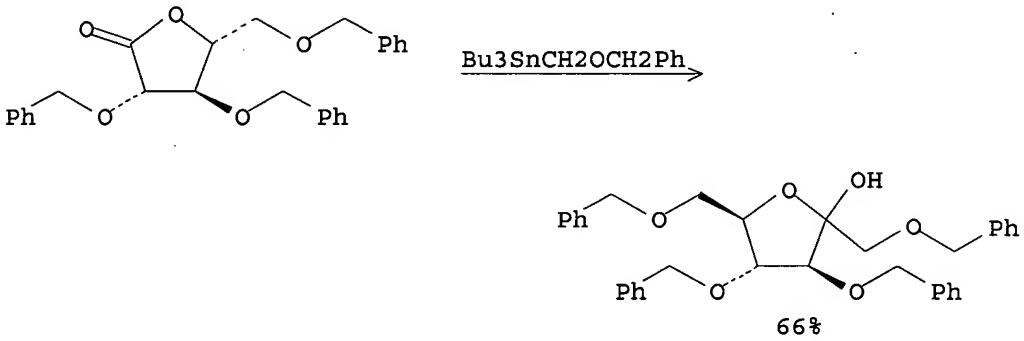
RX(5) OF 10



REF: Journal of Organic Chemistry, 57(4), 1304-6; 1992

L3 ANSWER 16 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

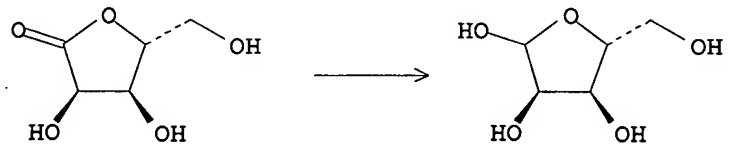
RX(1) OF 1



REF: Carbohydrate Research, 214(1), 187-92; 1991

L3 ANSWER 17 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

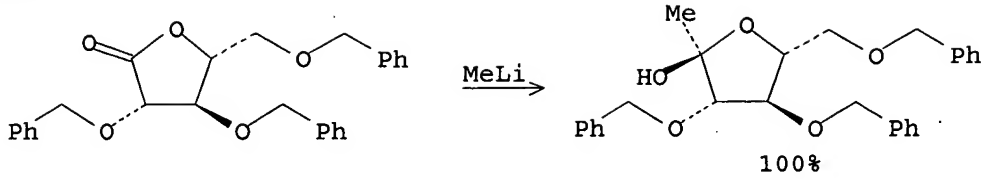
RX(1) OF 1



REF: Pol., 134957, 25 Jul 1986

L3 ANSWER 18 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(1) OF 9



REF: Journal of the Chemical Society, Chemical Communications, (16), 1085-6; 1989

L3 ANSWER 19 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(5) OF 14

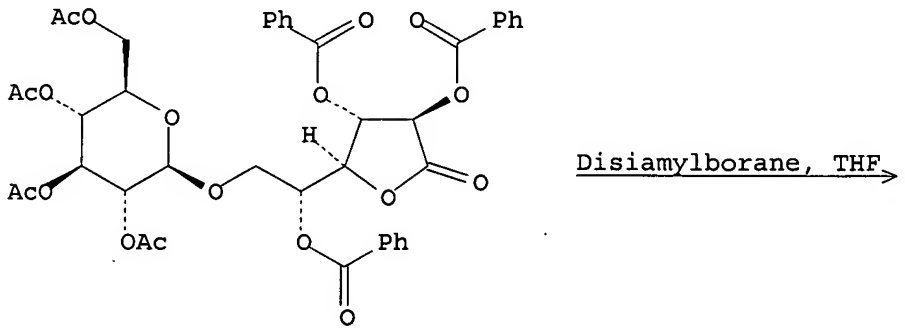
REF: Carbohydrate Research, 191(1), 130-7; 1989

L3 ANSWER 20 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

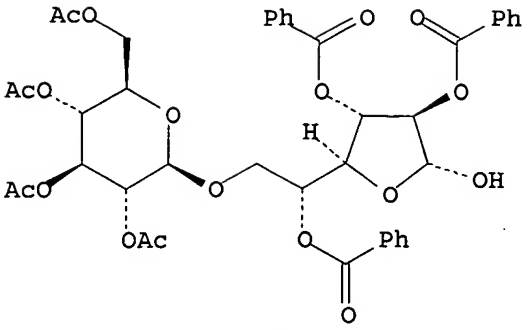
RX(13) OF 36 - REACTION DIAGRAM NOT AVAILABLE

L3 ANSWER 21 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(6) OF 21



RX(6) OF 21



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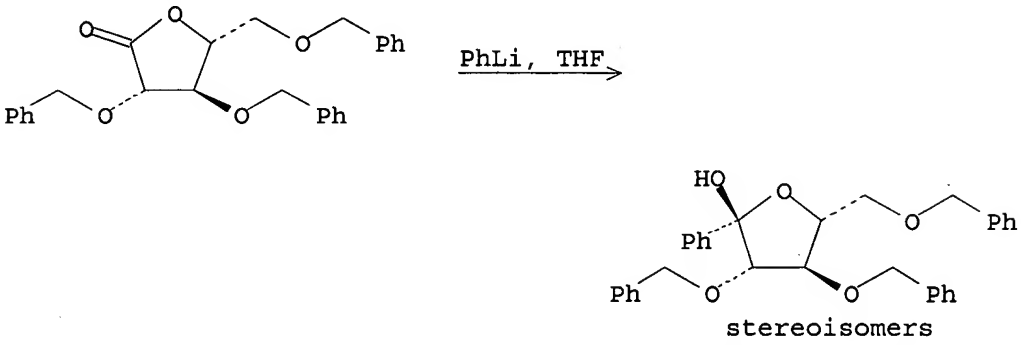
REF: Carbohydrate Research, 189,, 79-86; 1989

L3 ANSWER 22 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(7) OF 24

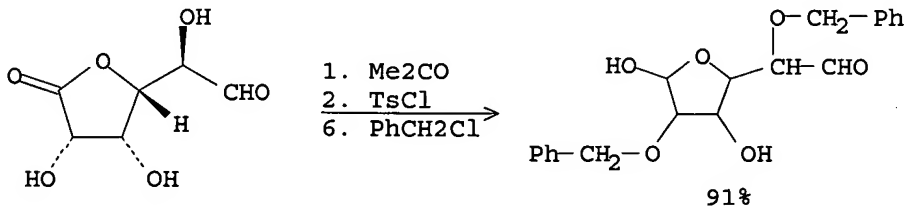


stereoisomers

REF: Journal of Organic Chemistry, 54(3), 610-12; 1989

L3 ANSWER 23 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(82) OF 183 - 7 STEPS

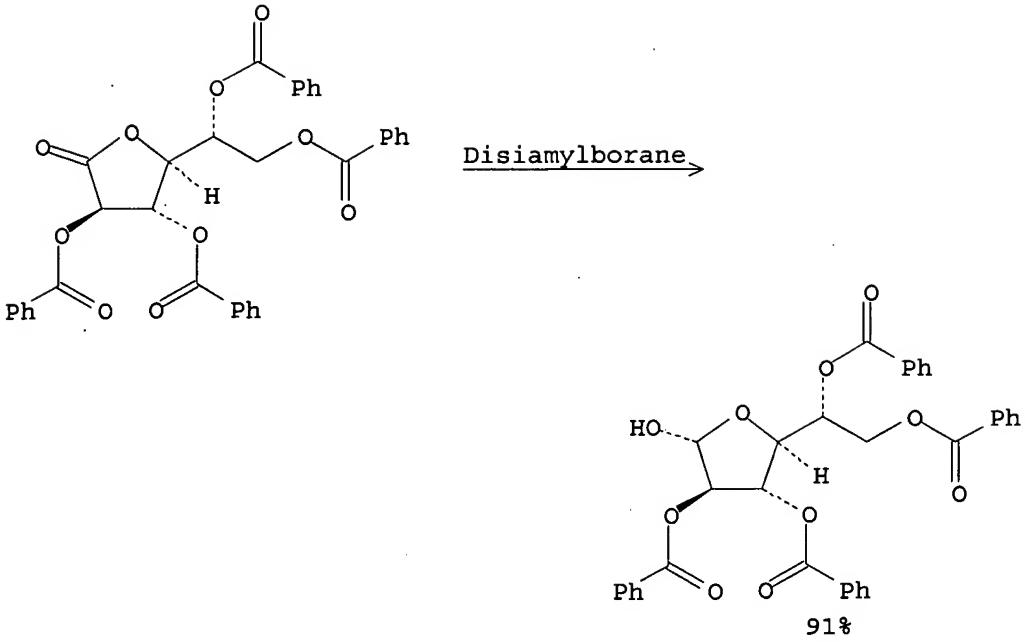


91%

REF: Chemistry Letters, (1), 123-6; 1987
NOTE: 3) 88% overall

L3 ANSWER 24 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

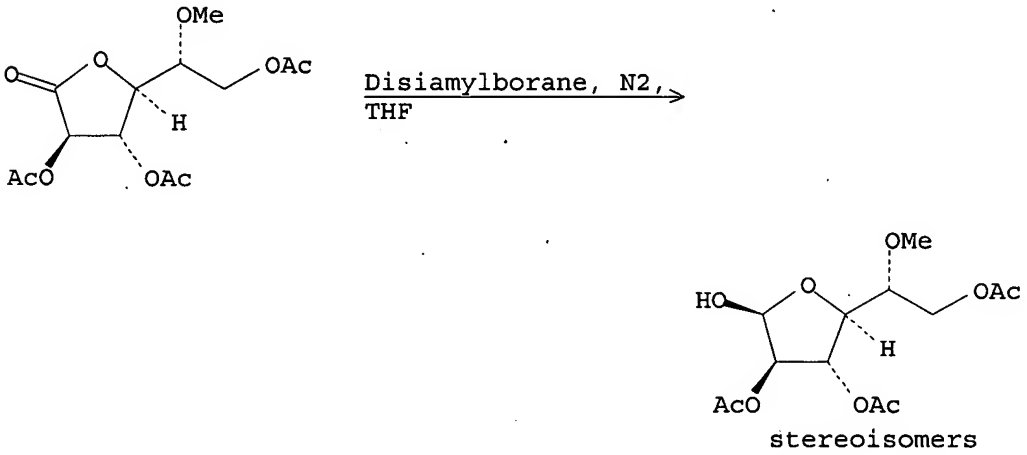
RX(1) OF 17



REF: Carbohydrate Research, 155,, 247-51; 1986

L3 ANSWER 25 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

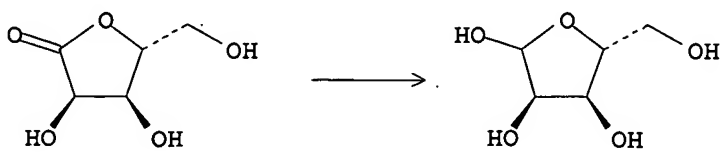
RX(5) OF 20



REF: Carbohydrate Research, 146(2), 233-40; 1986

L3 ANSWER 26 OF 26 CASREACT COPYRIGHT 2006 ACS on STN

RX(1) OF 3



REF: Pol., 121507, 30 Nov 1983

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L1                STRUCTURE UPLOADED
L2              4 S L1 SSS SAM
L3             26 S L1 SSS FULL
L4              0 S L3 AND (NAHTE OR SMI2)
L5              0 S L3 AND TELLUROHYDRIDE
L6              0 S L3 AND (SAMARIUM(A)IODIDE)
L7              0 S L3 AND (HYDROGEN(A)PALLADIUM(A)PHOSPHINE)
L8              0 S L3 AND (HYDROGEN(A)CATALYST)
L9              0 S L3 AND (ALUMINUM(W)T-BUTOXY(W)HYDRIDE)
```

Roy L. Whistler and J. N. BeMiller
Methods in Carbohydrate Chemistry, 1963, 2, 484–485

$[\alpha]^{20}_D$ +34° (*5*) and m.p. 145° (*7*). Various crystalline salts have been prepared (*1*), but they do not always give distinguishing melting points.

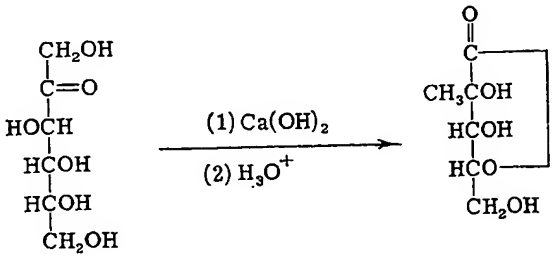
References

(*1*) See J. C. Sowden, *Advances in Carbohydrate Chem.*, **12**, 35 (1957).
(*2*) H. Kiliani, *Ber.*, **16**, 2625 (1883).
(*3*) H. Kiliani and H. Sanda, *Ber.*, **26**, 1649 (1893).
(*4*) H. Kiliani and P. Loeffler, *Ber.*, **37**, 1196 (1904); H. Kiliani and H. Naegell, *Ber.*, **35**, 3528 (1902); H. Kiliani, *Ber.*, **44**, 109 (1911).
(*5*) J. U. Nef, *Ann.*, **376**, 1 (1910).
(*6*) L. M. Utkin and G. O. Grabilina, *Doklady Akad. Nauk S.S.S.R.*, **93**, 301 (1953).
(*7*) H. Kiliani and F. Eisenlohr, *Ber.*, **42**, 2603 (1909).

[118] "α"-D-Glucosaccharino-1,4-lactone

2-*C*-Methyl-D-*ribo*-pentono-1,4-lactone from D-Fructose

By Roy L. Whistler and J. N. BeMiller
Department of Biochemistry, Purdue University, Lafayette, Indiana



(I) (II)

Introduction

"α"-D-Glucosaccharino-1,4-lactone (2-*C*-methyl-D-*ribo*-pentono-1,4-lactone) (II) (*1*) is prepared by the action of calcium hydroxide on D-fructose (I) (*2*) or "inverted" sucrose (*3*, *4*). The yields in either case are about the same.

Procedure

To a solution of 100 g. of β-D-fructose[1] (I) in 1 liter of boiled water is added 10 g. of calcium hydroxide. The mixture is flushed with nitrogen (footnote 1, Vol. II [115]) and kept 14 days at room temperature with frequent shaking, after which time an additional 40 g. of calcium hydroxide is

[1] "Inverted" sucrose may also be used (*3*, *4*).

added. The mixture is again flushed with nitrogen and kept 6–8 weeks at room temperature with occasional shaking.[2] The mixture is filtered, and the filtrate is saturated with carbon dioxide and filtered again. A concentrated aqueous solution of 38 g. of oxalic acid dihydrate[3] is then added with vigorous stirring. The mixture is warmed on a steam bath and filtered. The remaining calcium ions are removed by passing the filtrate through a column of 175 ml. of Amberlite IR-120(H+). The column is washed until the effluent is neutral. The decationized solution and washings are concentrated under reduced pressure to a thin sirup which is placed in a refrigerator for crystallization.[4] After several days, the crystals of "α"-D-glucosaccharino-1,4-lactone (II) are filtered from the mother liquor and recrystallized from water; yield about 10 g., m.p. 160–161°, $[\alpha]^{20}_D$ +93° (water) (*2, 5*).

Derivatives

Reported derivatives include the phenylhydrazide (*5, 6*) m.p. 167–169°, $[\alpha]^{20}_D$ +50° (water), the "anilide" (*7*), m.p. 193–195°, $[\alpha]^{20}_D$ +58° (water), $[\alpha]^{25}_D$ +55° (95% ethanol), and the anhydrobenzimidazole, 2-(1,4-anhydro-1-*C*-methyl-D-*ribo*-tetrahydroxybutyl)benzimidazole (*8*), m.p. 240–241°. The crystalline mono-*O*-isopropylidine derivative has also been prepared (*9*). Various crystalline salts have been reported (*4*), but they do not always give distinguishing melting points.

References

(*1*) J. C. Sowden and D. R. Strobach, *J. Am. Chem. Soc.*, 82, 3707 (1960).
(*2*) (*a*) C. Scheibler, *Ber.*, 13, 2212 (1880); (*b*) E. Peligot, *Compt. rend.*, 90, 1141 (1880).
(*3*) H. Kiliani, *Ber.*, 15, 701, 2953 (1882); *Ann.*, 218, 361 (1883).
(*4*) See J. C. Sowden, *Advances in Carbohydrate Chem.*, 12, 35 (1957).
(*5*) J. U. Nef, *Ann.*, 376, 1 (1910).
(*6*) E. Fischer and F. Passmore, *Ber.*, 22, 2728 (1889).
(*7*) J. W. Green, *J. Am. Chem. Soc.*, 78, 1894 (1956).
(*8*) J. C. Sowden and D. J. Kuenne, *J. Am. Chem. Soc.*, 75, 2788 (1953).
(*9*) L. M. Utkin and G. O. Grabilina, *Doklady Akad. Nauk S.S.S.R.*, 93, 301 (1953); J. C. Sowden, M. G. Blair, and D. J. Kuenne, *J. Am. Chem. Soc.*, 79, 6450 (1957).

[2] The long period of standing at room temperature can be replaced by several-hours heating at 100° (*2a*), but the yield obtained by this method is unsatisfactory (*3*).

[3] An amount of oxalic acid which is about 90% of that required to remove all the calcium ions in the filtrate should be added. This amount may vary and should be determined on an aliquot of the filtrate for each preparation.

[4] Frequently, seed crystals are needed. These may be obtained by extracting a portion of the sirup in a continuous extractor for 24 hr., concentrating the extract to a sirup, and crystallizing the sirup from ethyl acetate by the addition of petroleum ether (30–60°).

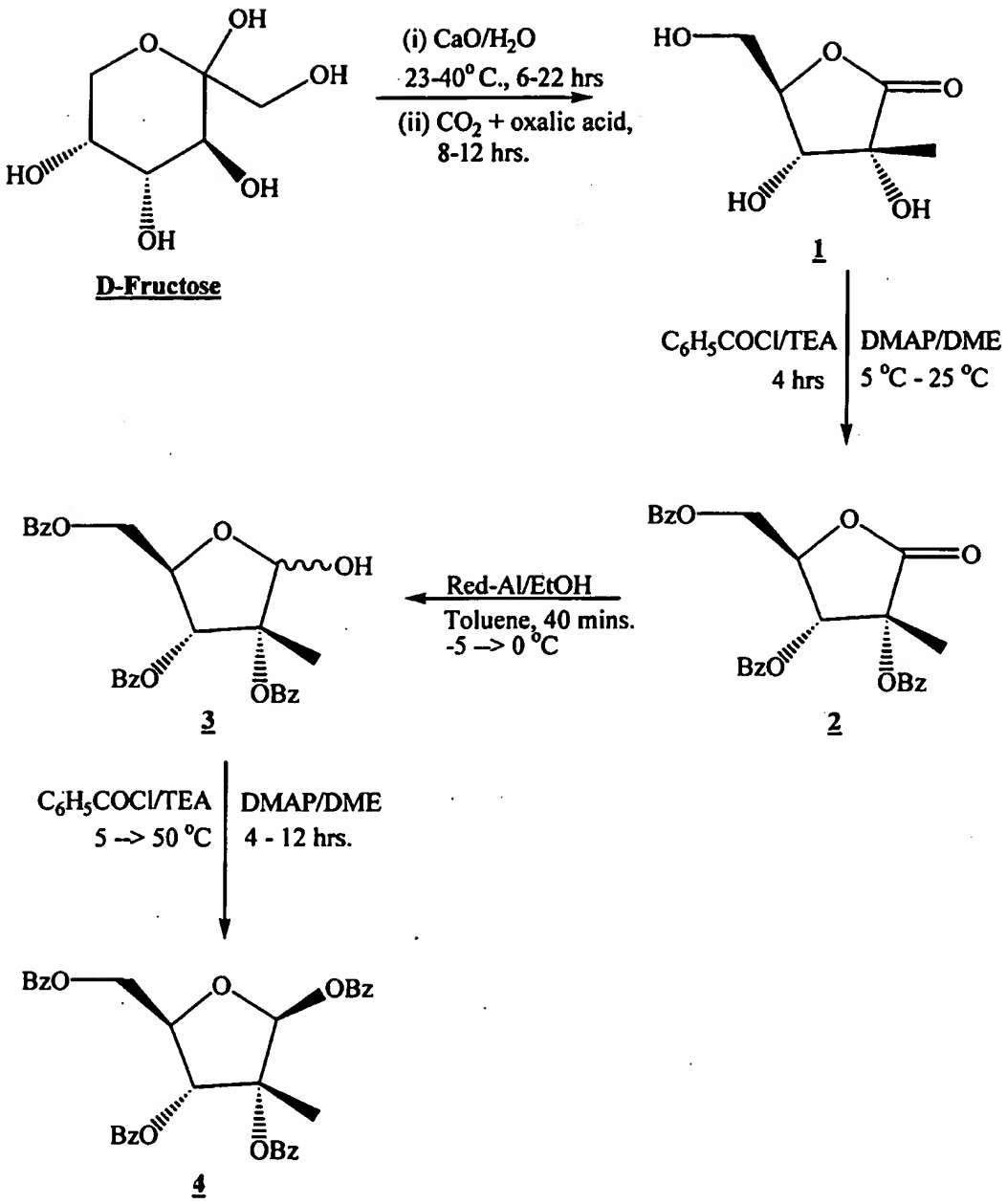
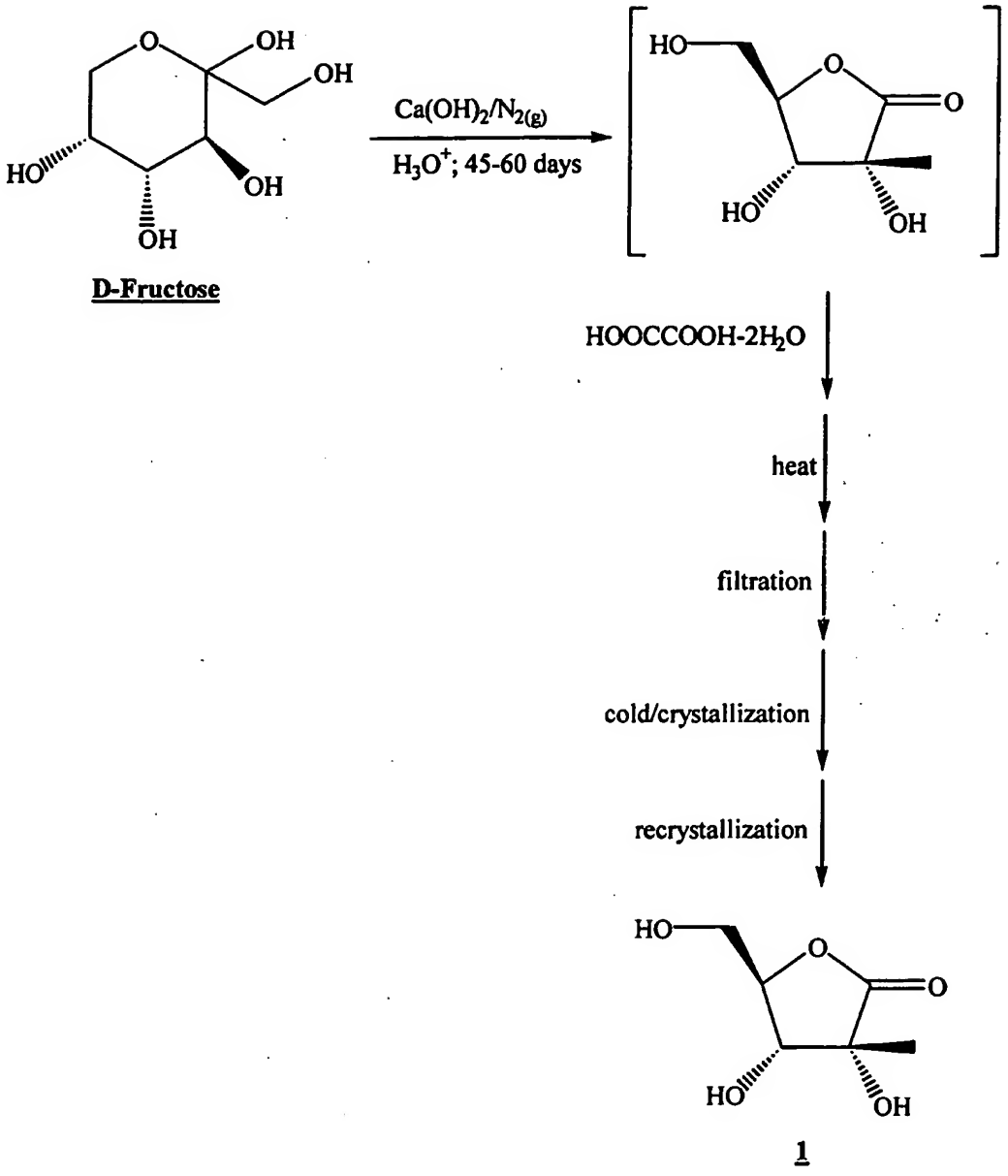

OH
O
OH
HO
OH
OH
D-Fructose
(i) CaO/H2O
23-40° C., 6-22 hrs
(ii) CO2 + oxalic acid,
8-12 hrs.
HO
O
O
HO
OH
1
C6H5COCl/TEA
4 hrs
DMAP/DME
5 °C - 25 °C
BzO
O
O
BzO
OBz
2
Red-Al/EtOH
Toluene, 40 mins.
-5 --> 0 °C
BzO
O
OH
BzO
OBz
3
C6H5COCl/TEA
5 --> 50 °C
DMAP/DME
4 - 12 hrs.
BzO
O
OBz
BzO
OBz
4

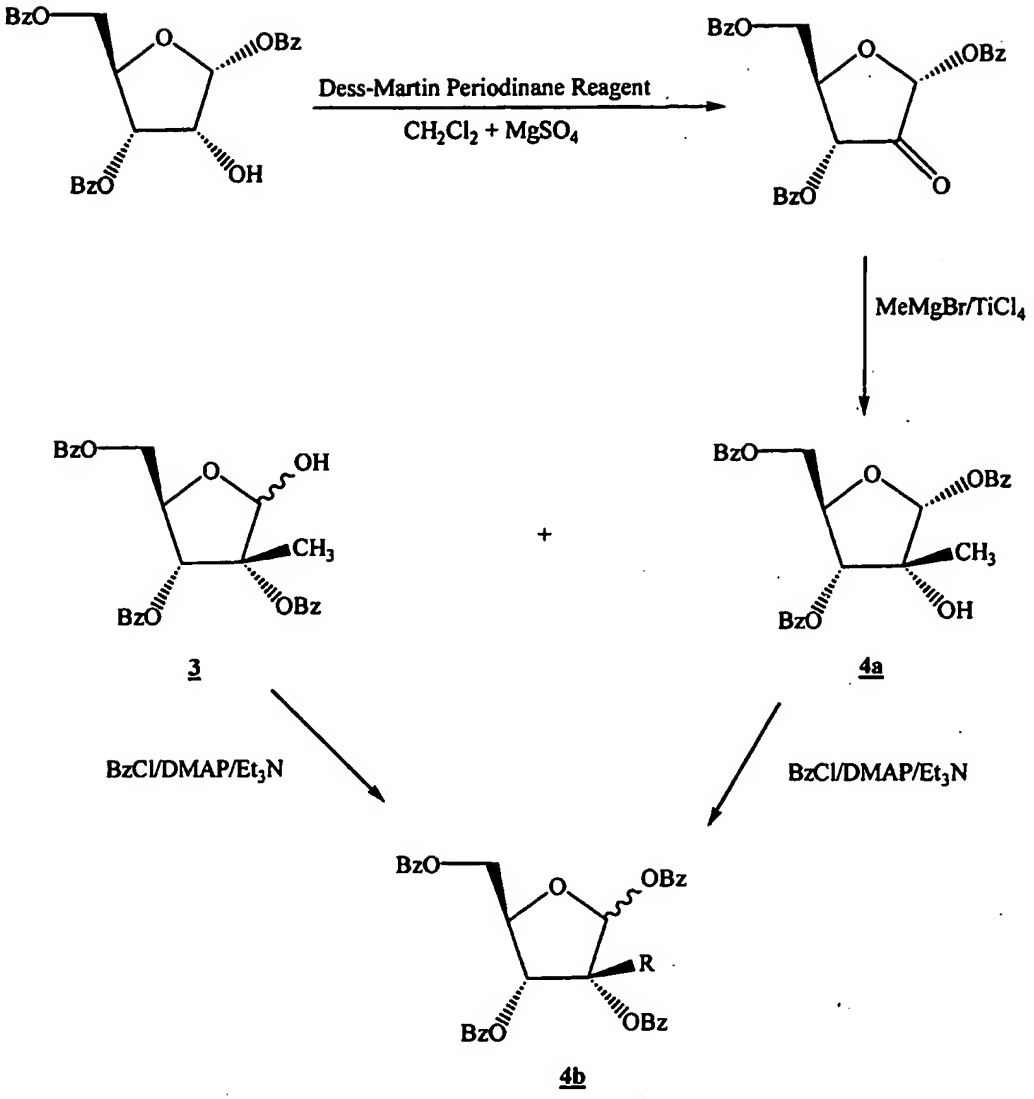
FIGURE 1



D-Fructose

1

FIGURE 2



Taken from Harry-O'kuru et al., J. Org. Chem., 1997, 62(6):1754-59.

FIGURE 3

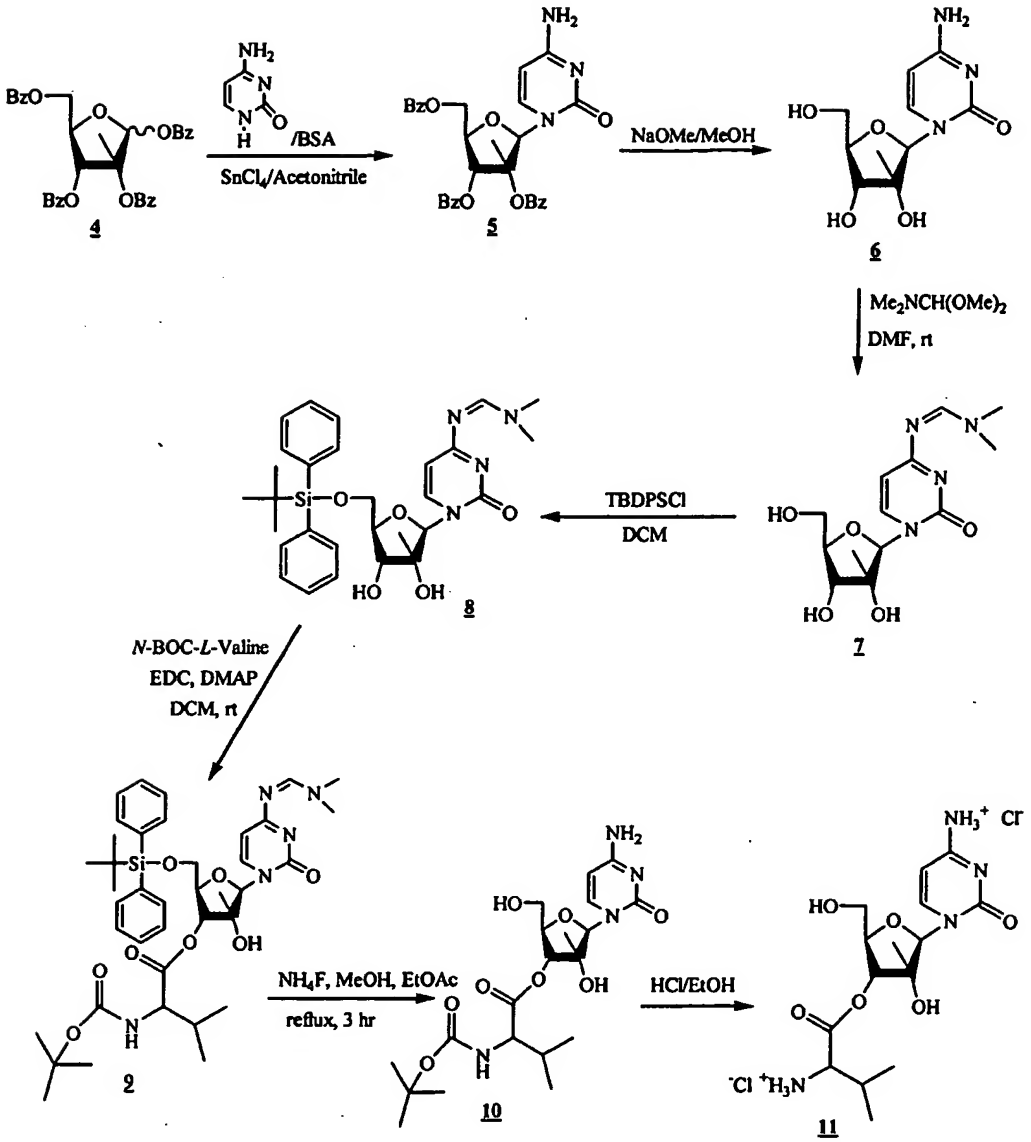

BzO
OBz
BzO
OBz
4
/BSA
SnCl4/Acetonitrile
5
NaOMe/MeOH
HO
OH
6
Me2NCH(OMe)2
DMF, rt
7
TBDPSCl
DCM
8
N-BOC-L-Valine
EDC, DMAP
DCM, rt
9
NH4F, MeOH, EtOAc
reflux, 3 hr
10
HCl/EtOH
11

FIGURE 4

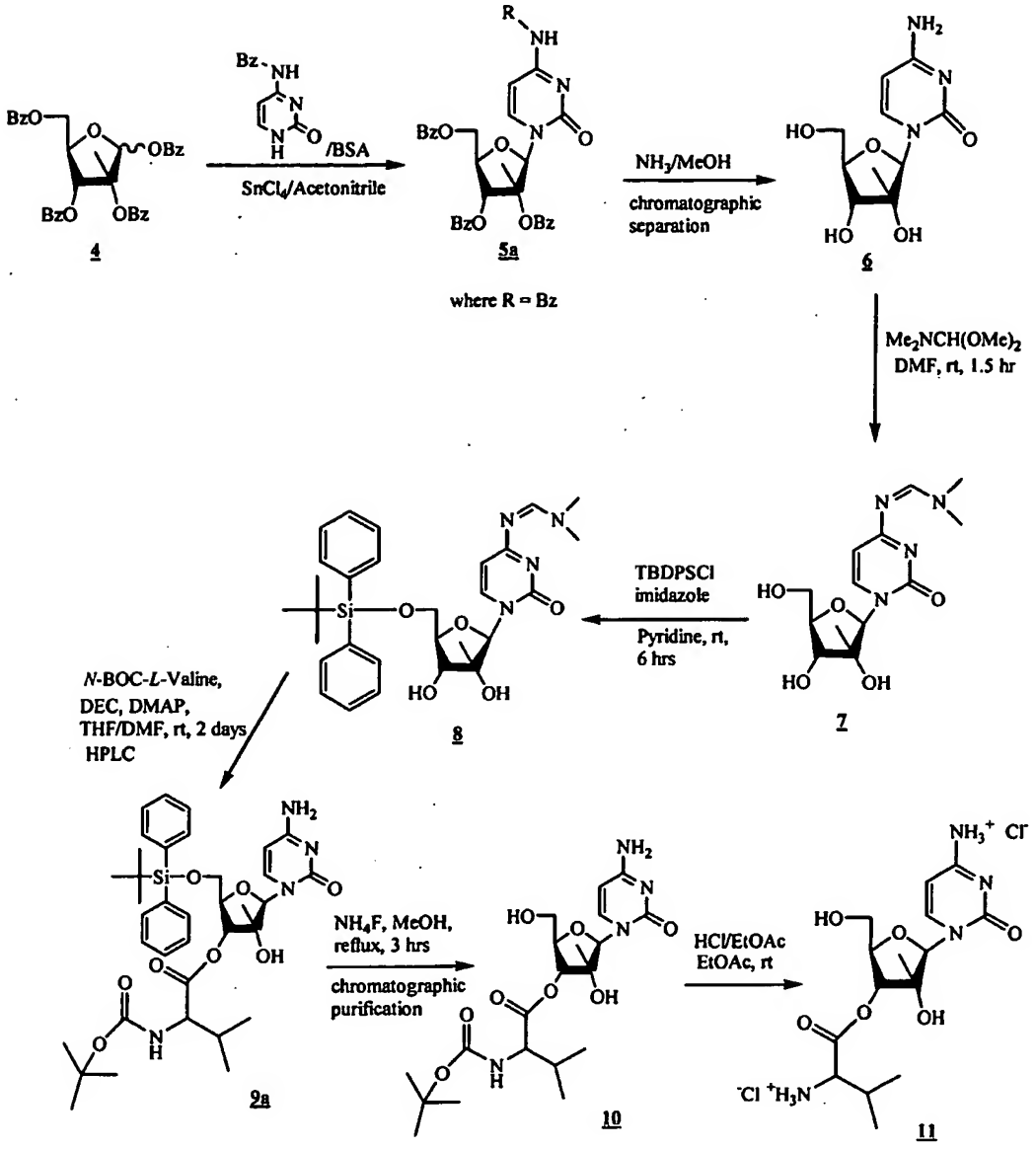

BzO
OBz
BzO
OBz
4
Bz
NH
/BSA
SnCl4/Acetonitrile
R
NH
BzO
OBz
5a
where R = Bz
NH3/MeOH
chromatographic separation
NH2
HO
OH
6
Me2NCH(OMe)2
DMF, rt, 1.5 hr
TBDPSCl
imidazole
Pyridine, rt, 6 hrs
8
7
N-BOC-L-Valine,
DEC, DMAP,
THF/DMF, rt, 2 days
HPLC
9a
NH4F, MeOH,
reflux, 3 hrs
chromatographic purification
10
HCl/EtOAc
EtOAc, rt
NH3+ Cl-
11

FIGURE 5

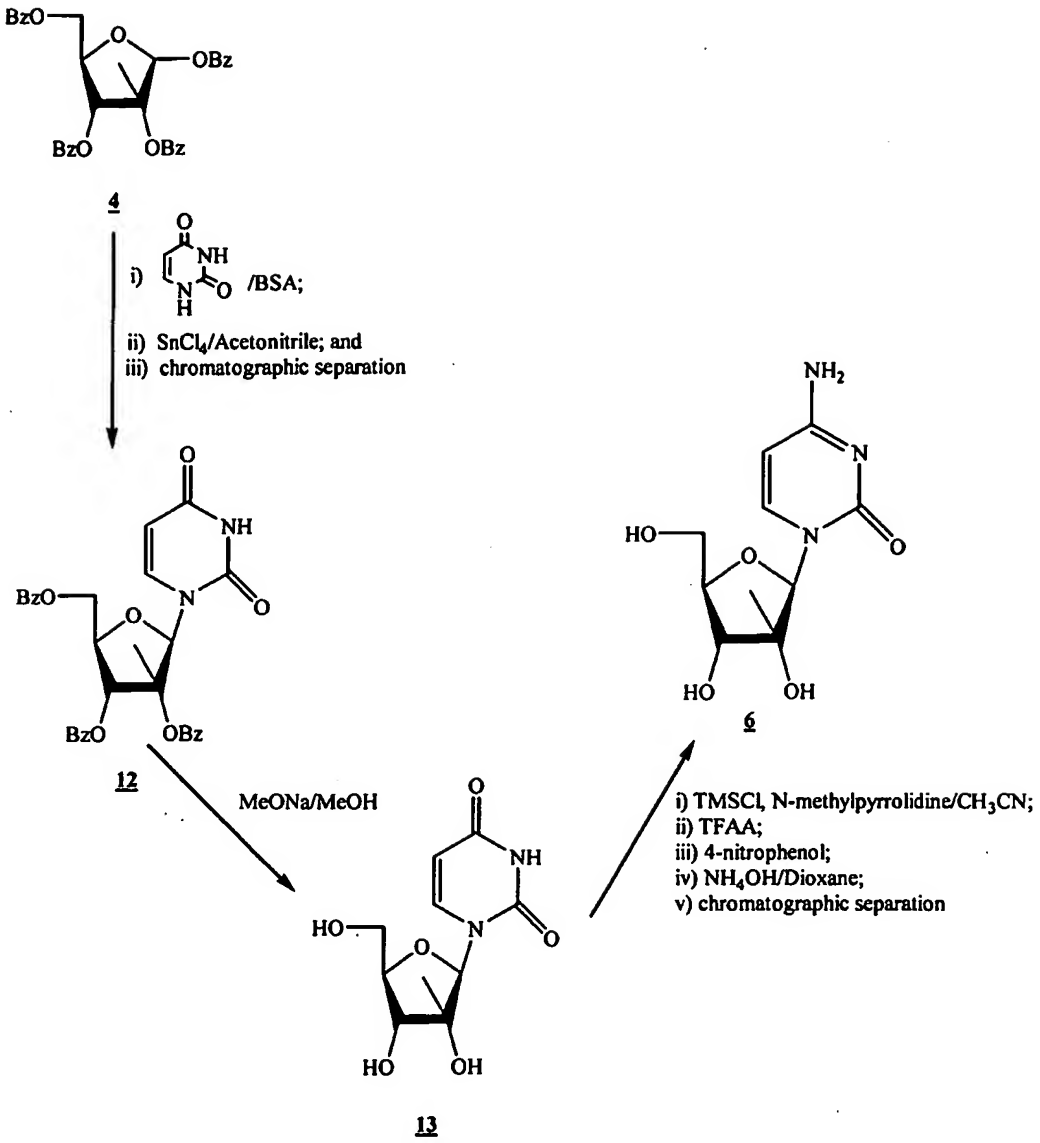

BzO
OBz
BzO
OBz
4
i) /BSA;
ii) SnCl4/Acetonitrile; and
iii) chromatographic separation
12
MeONa/MeOH
13
i) TMSCl, N-methylpyrrolidine/CH3CN;
ii) TFAA;
iii) 4-nitrophenol;
iv) NH4OH/Dioxane;
v) chromatographic separation
6

FIGURE 6